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The work completed during this period has been carried out by many co workers supported by the ONR and has been reported in published papers and more than 50 Technical Reports.

The people involved have been both graduate students and post doctoral fellows.

M. Schauer	(GS)	K. S. Law	(PD)
J. Wana	(PD)	H.S. Im	(GS)
J.A. Menapace	(GS)	P.J. Breen	(PD)
V.H. Grassian	(PD)	J.A. Warren	(PD)
S. Li	(PD)	R. Nowak	(PD)
M.R. Nimlos	(PD)	M.A. Young	(PD)

Just to put all this work together in one report below are the abstracts of the published and to be published papers from this work. They include studies of the structure of non rigid molecules, the formation of clusters and dimers, liquid cluster structure chemical reaction studies, and studies of cluster dynamics.

1984 to present: see attached.

Papers in press but not published: see attached.

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# Molecular jet study of aniline-helium van der Waals molecules and aniline radiationless relaxation in the ${}^1B_2$ excited electronic state<sup>a)</sup>

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(Received 9 May 1983; accepted 15 September 1983)

Fluorescence excitation (FE), dispersed emission (DE), and time of flight mass spectroscopy (TOFMS) techniques are employed to study the van der Waals molecules formed in a molecular supersonic jet of aniline and helium (AnHe<sub>x</sub>). It is found that AnHe<sub>1</sub>, AnHe<sub>2</sub>, and AnHe<sub>3</sub> have absorption bands that fall under all the An ( $\nu'$ ) vibronic features in the  ${}^1B_2$  electronic state of An. The features to the high energy side of the An vibronic transitions are tentatively associated with vibrations of the above van der Waals molecules. The DE from both An and AnHe<sub>x</sub> can be characterized as either "relaxed" or "unrelaxed" depending on whether or not the aniline vibronic state emitting is the same as or different from that which was pumped. All "relaxed" An emission can be associated with vibrational predissociation of the AnHe<sub>x</sub> species. All "unrelaxed" emission from AnHe<sub>x</sub> ( $\nu' + \nu$ ), with  $\nu' = \text{An mode}$  and  $\nu = \text{vdW bond mode}$ , can be associated with  $\Delta\nu = 0$  transitions from AnHe<sub>x</sub>. A number of other relaxation mechanisms are presented and discussed including collisional ones. Some time estimates for the major processes can be discussed.

## Molecular supersonic jet studies of aniline solvation by helium and methane<sup>a)</sup>

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(Received 31 August 1983; accepted 6 October 1983)

The technique of two color resonant two photon ionization coupled with time of flight mass spectroscopy has been employed to study aniline-He (AnHe<sub>x</sub>) and aniline-CH<sub>4</sub> (An(CH<sub>4</sub>)<sub>x</sub>) van der Waals clusters generated in a supersonic molecular jet. This technique allows identification of spectroscopic transitions with clusters of known mass because no ion fragmentation is observed. Specific features in the optical fluorescence excitation and dispersed emission spectra can thereby be uniquely identified with a particular cluster. Cluster vibrations can be analyzed by a Morse potential to yield the An-He bond dissociation energy  $D_0 \sim 100 \pm 50 \text{ cm}^{-1}$ . Careful analysis of the dispersed emission from AnHe<sub>x</sub> suggests  $145 < D_0 < 155 \text{ cm}^{-1}$ . It is found that the van der Waals bond stretching frequency is nearly the same in the ground and excited states and that there is a strong propensity rule for  $\Delta V = 0$  ( $V = \text{vdW bond mode}$ ) as expected in this case, although  $\Delta V = \pm 1$  transitions can be observed. The AnHe<sub>1</sub> and AnHe<sub>2</sub> origins are slightly red shifted with respect to the An origins, while the AnHe<sub>x</sub> ( $x \geq 3$ ) origin is broad and nearly unshifted. This pattern is followed for An(CH<sub>4</sub>)<sub>x</sub> clusters; AnCH<sub>4</sub> transitions are red shifted 80  $\text{cm}^{-1}$  from the comparable An features and An(CH<sub>4</sub>)<sub>2</sub> transitions are 160  $\text{cm}^{-1}$  below their comparable An feature. The An(CH<sub>4</sub>)<sub>x</sub> ( $x \geq 3$ ) transitions appear at  $\sim 200\text{--}300 \text{ cm}^{-1}$  below their comparable An mode. The binding energy for the An-CH<sub>4</sub> bond is found to be  $500 < D_0 < 700 \text{ cm}^{-1}$  in the  ${}^1B_2$  state of aniline. Aniline has a strong preference for binding the solvent above and below the aromatic ring. Since the  $D_0$  is large for An-CH<sub>4</sub> and the stretching mode is only  $\sim 25 \text{ cm}^{-1}$  the An(CH<sub>4</sub>)<sub>x</sub> system builds up a large density of states in the van der Waals degrees of freedom. This density of states allows intramolecular vibrational redistribution (IVR) to take place, if the An mode excited is lower in energy than the  $D_0$  value. The rate of IVR from  $6a'$  ( $O_0^0 + 500 \text{ cm}^{-1}$ ) is somewhat faster than the 5 ns fluorescence rate but much slower than the rate of vibrational predissociation (VP) from higher levels. Both the IVR process, due to the van der Waals vibrational density of states, and the limiting solvent red shift, at a value similar to that found for cryogenic solutions, are discussed in terms of these clusters as model solute/solvent systems.

## → Brillouin scattering studies of the successive phase transitions in $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ <sup>a)</sup>

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(Received 30 September 1983; accepted 29 December 1983)

Brillouin scattering spectra are reported and analyzed for the layered perovskite compound  $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ . Particular attention has been given to successive phase transitions in this system:  $D_{4h}^{17} \leftrightarrow D_{2h}^{18} \rightleftharpoons D_{4h}^{16}$ . It is found that the elastic constant  $c_{66}$  is the major contributor to instabilities in this system. A two-dimensional order parameter at the Brillouin zone boundary  $X$  point is introduced into the Landau free-energy to account for this sequence of transitions. An additional secondary instability (one-dimensional order parameter) at the  $Z$  point is used to generate the  $D_{2h}^{18} \rightleftharpoons D_{4h}^{16}$  phase transition: inclusion of the two order parameters circumvents the need for postulating a  $D_{2h}^{10}$  phase between the  $D_{2h}^{18}$  and  $D_{4h}^{16}$  phases and for higher order temperature dependent terms in the free energy expansion. The  $D_{4h}^{17} \leftrightarrow D_{2h}^{18}$  phase transition is characterized by a strong Landau-Khalatnikov contribution to  $c_{66}$  and a large dynamical critical behavior.

## → Supersonic molecular jet studies of toluene-helium and toluene-methane clusters<sup>a)</sup>

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(Received 23 December 1983; accepted 8 March 1984)

The techniques of fluorescence excitation (FE), dispersed emission (DE), and one- and two-color time of flight mass spectroscopy (TOFMS) have been employed to study van der Waals clusters of toluene-helium (TolHe) and toluene-methane (TolCH<sub>4</sub>) formed in a supersonic molecular jet. Spectral shifts for the toluene  $^1B_2 \leftarrow ^1A_1$  transition have been characterized for TolHe<sub>1,2</sub> and Tol(CH<sub>4</sub>)<sub>1,2</sub>. The van der Waals stretching frequencies ( $\nu^1$ ) in the excited states of these clusters have been identified. The ground state stretch ( $\nu_1$ ) for TolHe has also been found; it is quite similar to the TolHe  $\nu^1$ . The binding energies ( $D_0$ ) for Tol-He clusters lie between 75 and 90 cm<sup>-1</sup> and those for Tol-CH<sub>4</sub> clusters lie between 533 and 739 cm<sup>-1</sup>. The coordination of a third solvent molecule to those clusters generates a broad spectrum whose shift is close to the limiting value for a large ( $x > 3$ ) cluster. A comparison between these data and methane solution data is presented.

## → Molecular jet study of the solvation of benzene by methane, ethane, and propane<sup>a)</sup>

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(Received 6 July 1984; accepted 1 October 1984)

Two color time of flight mass spectroscopy studies of benzene solvated by methane, ethane, and propane in a molecular jet have been carried out. Absorption has been characterized for both the 0<sub>0</sub><sup>0</sup> and 6<sub>0</sub><sup>0</sup> transitions of benzene (alkane)<sub>x</sub> ( $x = 1, 2, 3, \dots$ ). Atom-atom exponential-6 potentials have been employed to calculate cluster geometry and binding energy. Comparisons between calculations and experiments allow the identification of specific configurations for the cluster spectroscopic transitions. Cluster spectral shifts can also be identified and a correlation between the size of the cluster red shift and geometry has been developed. The closer the solvent is to the aromatic  $\pi$  system of the ring, the larger the red shift. Relative intensity data for different clusters has led to a clarification of cluster nucleation. Most clusters are formed by the interaction of solvent dimers or larger species with a solute molecule.

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## **Molecular jet study of the solvation of toluene by methane, ethane, and propane<sup>a</sup>**

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(Received 6 July 1984; accepted 1 October 1984)

Two color time of flight mass spectroscopy studies of toluene solvated by methane, ethane, and propane in a supersonic molecular jet have been carried out. This work is quite similar to the studies in the preceding paper on benzene. The conclusions and finding in the benzene investigation are strengthened and elaborated. The comparison of calculations and experiments has yielded information on binding energy, geometry, and spectral shift. A strong correlation is found between observed cluster transition intensity and cluster nucleation processes and a tentative nucleation scheme for the molecular jet formation of solute-solvent clusters is presented

## **Dimers of aromatic molecules: (Benzene)<sub>2</sub>, (toluene)<sub>2</sub>, and benzene-toluene<sup>a,b</sup>**

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(Received 1 June 1984; accepted 26 July 1984)

The optical absorption spectra of the first excited singlet states of the benzene, toluene, and toluene-benzene dimers, created in a supersonic molecular jet, are reported. The absorption spectra are detected through two-color time of flight mass spectroscopy; this method eliminates fragmentation of dimers and higher clusters and the dimer spectra are uniquely observed. The benzene dimer observed in this experiment is suggested to have a parallel stacked and displaced configuration of  $C_{2h}$  symmetry. Both the toluene and toluene-benzene dimers have two configurations: parallel stacked and displaced [based on (benzene)<sub>2</sub>] and perpendicular. (Benzene)<sub>2</sub>, (toluene)<sub>2</sub>, and toluene-benzene form excimers in the excited state for the parallel stacked displaced configurations. The transformation of (benzene)<sub>2</sub> to the excimer takes place at the  $0^0$  with a  $\sim 0 \text{ cm}^{-1}$  barrier while the excimer is formed for toluene-benzene with a  $\sim 900 \text{ cm}^{-1}$  barrier. An exciton analysis of the (benzene)<sub>2</sub>  $0_0^0$  and  $6_0^1$  yields  $M_{12}$ , the excitation exchange interaction, equal to  $\sim 1.6 \text{ cm}^{-1}$ .

## **Calculations of the geometry and binding energy of aromatic dimers: Benzene, toluene, and toluene-benzene<sup>a,b</sup>**

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Calculations of the geometries and energies of the benzene, toluene, and toluene-benzene dimers using a combination of atom-atom and multipolar potentials are presented and discussed. An exponential-six atom-atom potential plus a molecular quadrupole-quadrupole interaction term gives the reported parallel displaced  $C_{2h}$  benzene dimer geometry. The excited state behavior of the benzene dimer can be qualitatively understood based on this calculation. The toluene-benzene dimer is well modeled by these terms in addition to a dipole-quadrupole interaction term. Both parallel displaced and perpendicular configurations are obtained in agreement with the experimental data. Using exponential-six dipole-dipole, quadrupole-quadrupole, and dipole-quadrupole interactions the toluene dimer can be satisfactorily modeled. The calculations generally suggest that excitation of parallel displaced dimers can lead to rearrangement (and possible excimer formation) in the excited state.

## Molecular jet study of van der Waals complexes of flexible molecules: *n*-Propyl benzene solvated by small alkanes<sup>a)</sup>

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(Received 27 August 1984; accepted 28 November 1984)

A combination of atom-atom potential calculations and experimental molecular jet spectroscopic studies is used to elucidate the geometry and binding energy of *n*-propyl benzene/methane, ethane, and propane clusters. Two color time-of-flight mass spectroscopy data and calculations are presented for both *trans* and *gauche* configurations of *n*-propyl benzene with up to three hydrocarbon molecules of solvation. Cluster shifts and geometry are treated in detail for the observed and calculated systems. Solvation, as observed in the clusters, seems to have little effect on the geometry of the solute in this instance. Alkyl chain motion is also discussed for the *n*-propyl benzene isolated molecule.

## Molecular jet study of solvation of pyrazine by small hydrocarbons<sup>a)</sup>

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(Received 28 March 1985; accepted 3 October 1985)

Supersonic molecular jet 2-color time-of-flight mass spectroscopy studies are reported for pyrazine solvated by methane, ethane, and propane. The results parallel those obtained for benzene and toluene solvated by these molecules. The presence of nitrogen atoms and lone pair electrons in the aromatic system has only a small effect on the cluster structure. Lennard-Jones potential calculations are presented along with the experimental data. Cluster shifts and binding energies are reported and correlated with geometries. The nucleation process for cluster formation appears to involve solvent dimers, as was found for the aromatic hydrocarbon systems.

## Supersonic molecular jet studies of toluene-helium and toluene-methane clusters<sup>a)</sup>

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(Received 23 December 1983; accepted 8 March 1984)

The techniques of fluorescence excitation (FE), dispersed emission (DE), and one- and two-color time of flight mass spectroscopy (TOFMS) have been employed to study van der Waals clusters of toluene-helium (TolHe) and toluene-methane (TolCH<sub>4</sub>) formed in a supersonic molecular jet. Spectral shifts for the toluene <sup>1</sup>B<sub>2</sub> ← <sup>1</sup>A<sub>1</sub> transition have been characterized for TolHe<sub>1,2</sub> and Tol(CH<sub>4</sub>)<sub>1,2</sub>. The van der Waals stretching frequencies (*V*<sup>1</sup>) in the excited states of these clusters have been identified. The ground state stretch (*V*<sub>1</sub>) for TolHe has also been found; it is quite similar to the TolHe *V*<sup>1</sup>. The binding energies (*D*<sub>0</sub>) for Tol-He clusters lie between 75 and 90 cm<sup>-1</sup> and those for Tol-CH<sub>4</sub> clusters lie between 533 and 739 cm<sup>-1</sup>. The coordination of a third solvent molecule to those clusters generates a broad spectrum whose shift is close to the limiting value for a large (*x* > 3) cluster. A comparison between these data and methane solution data is presented.

# Hydrogen bonded and non-hydrogen bonded van der Waals clusters: Comparison between clusters of pyrazine, pyrimidine, and benzene with various solvents <sup>a)</sup>

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(Received 13 December 1985; accepted 1 May 1986)

Solute-solvent clusters of pyrazine, pyrimidine, and benzene (solutes) and  $C_nH_{2n-2}$  ( $n = 1, 2$ ),  $NH_3$ , and  $H_2O$  (solvents) are studied by the techniques of supersonic molecular jet spectroscopy and two-color time-of-flight mass spectroscopy (two-color TOFMS). Spectral shifts, van der Waals (vdW) modes, dissociation energies, and vdW mode-solute mode vibronic couplings are characterized for most of the observed clusters. Based on these data and previous results for hydrocarbon systems, cluster geometries can be suggested. Lennard-Jones potential (6-12-1) calculations are also performed for these clusters and in all instances for which comparisons can be readily made, calculated and experimentally estimated geometries and binding energies agree completely. Clusters of *N*-heterocyclic solutes and  $H_2O$  are not observed experimentally. Systematics and trends among the clusters reported herein and those previously reported are discussed and analyzed.

## Calculation of the Vibronic Structure of Solute/Solvent van der Waals Clusters

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Calculations of the eigenvectors and eigenvalues for the intermolecular vibrational modes of van der Waals clusters of benzene(Ar)<sub>1</sub>, -(CH<sub>4</sub>)<sub>1</sub>, -(H<sub>2</sub>O)<sub>1</sub>, and -(NH<sub>3</sub>)<sub>1</sub> and *s*-tetrazine(Ar)<sub>1</sub> are presented. The calculations are based on an atom-atom Lennard-Jones (6-12-1-10-12) potential function, which includes hydrogen bonding, and a normal coordinate analysis. The clusters are treated as "giant molecules". The results of these calculations are then used to assign the van der-Waals vibronic spectra of the above clusters. Agreement between calculations and experiments is excellent for binding energies, symmetries, and van der Waals frequencies. The  $S_1 \leftarrow S_0$  vibronic transitions of the above clusters are essentially completely assigned based on these calculations. A major conclusion of this work is that the low-frequency van der Waals torsions and bends are active in Herzberg-Teller vibronic coupling. A number of approximate diatomic molecule calculations are compared to the above procedure and thereby evaluated.

## The $S_2 \leftarrow S_0$ laser photoexcitation spectrum and excited state dynamics of jet-cooled acetophenone<sup>a)</sup>

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The  $S_2 \leftarrow S_0$  photoexcitation spectrum of jet-cooled acetophenone is presented. The observed homogeneously broadened linewidths indicate  $S_2$  lifetimes  $< 0.26$  ps while the measured emission lifetimes range from  $540 \pm 30$  ns for  $S_2$   $0_0^0$  excitation to  $130 \pm 50$  ns for  $S_2$   $12_1^1$  excitation. The dynamics revealed by the spectrum are discussed in terms of the known photochemical and photophysical rates of the excited states of acetophenone. Arguments are presented which identify the emitting state as a known triplet state of acetophenone.

## On the pyrazine and pyrazine-pyrimidine dimers<sup>a)</sup>

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(Received 9 April 1986; accepted 6 June 1986)

Spectra of the pyrazine- $d_4$ , pyrazine- $h_4$ -pyrazine- $d_4$ , and pyrazine- $d_4$ -pyrimidine dimer are obtained and analyzed with the help of Lennard-Jones-hydrogen-bonding (LJ-HB) potential energy calculations. The pyrazine isotopic hetero and homo dimers possess nearly identical spectra with the exception that the perpendicular dimer features are displaced to the red by  $\sim 11$   $\text{cm}^{-1}$ . Exchange or exciton interactions in this system are vanishingly small (less than  $1 \text{ cm}^{-1}$ ). The geometries suggested by the isotopically substituted pyrazine dimer spectra are the same as those found for the pyrazine- $h_4$  homo dimer: a parallel planar hydrogen bonded and a perpendicular dimer. The pyrazine- $d_4$ - and pyrazine- $h_4$ -pyrimidine dimer spectra are quite complicated. These spectra can be assigned as arising from one parallel stacked head-to-tail displaced dimer, one parallel planar dimer, and three perpendicular dimers based on comparisons with spectra of the pyrazine and pyrimidine dimers.

## On the phase transition in *N*-isopropylcarbazole

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(Received 27 May 1986; accepted 29 July 1986)

The elastic properties of *N*-isopropylcarbazole (NIPC), a pyroelectric molecular crystal, are investigated by Brillouin scattering. The full elastic constant tensor is determined at 295 K and the temperature dependences of the elastic constants are given. The major experimental finding reported is the anomaly of the LA  $a$ -axis mode governed by the  $c_{11}$  elastic constant. This mode exhibits a pronounced downward bending on both sides of the nonferroic, first order phase transition at  $\sim 137$  K. Symmetry allowed linear-quadratic and biquadratic couplings between the Brillouin zone boundary one-dimensional order parameter and the zone center strain introduced into the Landau free energy do not account for the observed anomaly. The transition is characterized in terms of a strong dispersion of the  $c_{11}$  elastic constant and a large dynamical critical behavior. By combining the  $c_{11}$  elastic constant data and the Brillouin scattering LA  $a$ -axis mode half-width data through a Landau-Khalatnikov process, one can extract a relaxation time satisfying a mean-field dependence characteristic of critical slowing down of the order parameter.

## An RRKM Approach to Vibrational Predissociation of van der Waals Clusters

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Vibrational predissociation (VP) rates are calculated for the *s*-tetrazine-Ar van der Waals complex excited to various vibronic levels of the first excited singlet state by employing RRKM theory and a serial mechanism for intramolecular vibrational redistribution (IVR) and VP. In the model presented, VP cannot take place from the optically accessed zero-order tetrazine vibronic state but follows only after IVR has populated the van der Waals modes with more energy than the cluster binding energy. The calculations can be compared with two published studies of the IVR and VP processes in the *s*-tetrazine-Ar cluster: a picosecond study of the time evolution of vibronic emission from the cluster and the free molecule following cluster excitation; and a CW emission intensity study of the cluster and free molecule following cluster excitation. Agreement between the calculation and the available experimental data is semiquantitative and as good as the agreement between the two experimental studies reported (approximately a factor of two).



## Spectroscopic studies of cryogenic fluids: Benzene in propane<sup>a)</sup>

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Energy shifts and bandwidths for the  ${}^1B_{2u} \rightarrow {}^1A_{1g}$  optical absorption and emission transitions of benzene dissolved in propane are presented as a function of pressure, temperature, and density. Both absorption and emission spectra exhibit shifts to lower energy as a function of density, whereas no shifts are observed if density is kept constant and temperature and pressure are varied simultaneously. Density is thus the fundamental microscopic parameter for energy shifts of optical transitions. The emission half-width is a linear function of both temperature and pressure but the absorption half-width is dependent only upon pressure. These results are interpreted qualitatively in terms of changes occurring in the intermolecular potentials of the ground and excited states. Both changes in shape of and separation between the ground and excited state potentials are considered as a function of density. Classical dielectric (Onsager-Böttcher), microscopic dielectric (Wertheim) and microscopic quantum statistical mechanical (Schweizer-Chandler) theories of solvent effects on solute electronic spectra are compared with the experimental results. Calculations suggest limited applicability of dielectric theories but good agreement between experiment and microscopic theory. The results demonstrate the usefulness of cryogenic solutions for high pressure, low temperature spectroscopic studies of liquids.

## Spectroscopic studies of cryogenic fluids: Benzene in nitrogen<sup>a)</sup>

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Energy shifts and bandwidths for the  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  optical absorption of benzene in supercritical nitrogen are presented as a function of pressure, temperature, and density. The pressure and density dependence of energy shifts of room temperature emission of benzene in nitrogen fluid is also reported. Both absorption and emission spectra exhibit shifts to lower energy as a function of density, whereas almost no spectral shifts are observed if the density is kept constant and temperature and pressure varied simultaneously. Thus, density is the fundamental microscopic parameter for energy shifts of optical transitions in supercritical nitrogen. This result is analogous to the findings for the liquid benzene/propane system and can be interpreted qualitatively in terms of changes occurring in the intermolecular potential; however, in the benzene/supercritical nitrogen system an additional small density independent temperature effect on the transition energy has been identified. Experimental results are compared to dielectric (Onsager-Böttcher and Wertheim) and microscopic quantum statistical mechanical (Schweizer-Chandler) theories of solvent effects on solute electronic spectra. Reasonably good agreement between experiment and theory is found. The results demonstrate that liquid state theory can be used to describe the supercritical nitrogen fluid.

## van der Waals Modes of Solute/Solvent Clusters: Benzene-Methane, -Deuteriomethane, and -Carbon Tetrafluoride

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Clusters of benzene( $\text{CD}_4$ )<sub>1</sub> and -( $\text{CF}_4$ )<sub>1</sub> are created in a supersonic molecular jet and are studied by two-color time-of-flight mass spectroscopy. The clusters'  $S_1 \leftarrow S_0$  intermolecular vibronic structures are characterized by calculational modeling of the clusters' intermolecular motion. The calculations include (1) an intermolecular normal-coordinate analysis (NCA) which treats all six van der Waals modes under a harmonic oscillator assumption and (2) a three-dimensional hindered rigid-rotor analysis (3D-HRRA) which treats the intermolecular torsional motion. Agreement between calculation and experiment is excellent for binding energy, symmetries, and van der Waals mode energies. The cluster spectra and calculated intermolecular modes are compared to those of benzene( $\text{CH}_4$ )<sub>1</sub> reported previously. A major conclusion of this work is that the clusters behave rigidly with regard to internal rotation of the cluster subunits and that the clusters possess unique equilibrium geometries. The internal torsional motion is oscillatory and is constrained by an orientationally dependent intermolecular potential whose barrier height is of the order of the cluster binding energy.

## A study of nonrigid aromatic molecules by supersonic molecular jet spectroscopy. I. Toluene and the xylenes

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Dispersed emission and time of flight mass spectra are presented for jet-cooled toluene, and *o*-, *m*-, and *p*-xylene. The spectra exhibit features, typically within  $100\text{ cm}^{-1}$  of the  $S_1 = S_0$  origins, which are assigned to transitions associated with the internal rotation of the ring methyl groups. A model is developed which treats this methyl motion as that of a one-dimensional rigid rotor. The spacings of the peaks in the spectra are used to solve for the rotational constant  $B$  of the methyl rotor, and for the size and shape of the  $n$ -fold barrier to rotation (i.e.,  $V_1$ ,  $V_n$ , etc.) within this model. For toluene and *p*-xylene, the barrier is found to be small in both the ground ( $S_0$ ) ( $V_n \sim 10\text{ cm}^{-1}$ ) and excited ( $S_1$ ) ( $V_n \sim 25\text{ cm}^{-1}$ ) electronic states. For *m*-xylene, the ground state is again found to have a low barrier ( $V_n \sim 25\text{ cm}^{-1}$ ), but the excited state has a potential barrier of  $V_1 = 81\text{ cm}^{-1}$ ,  $V_n = -30\text{ cm}^{-1}$ . The barrier to rotation of the ring methyl groups is observed to be the highest for *o*-xylene. In this case the ground state is found to have a rather large barrier  $V_1 = 425\text{ cm}^{-1}$ ,  $V_n = 18\text{ cm}^{-1}$  which changes to  $V_1 \sim 166\text{ cm}^{-1}$ ,  $V_n \sim -25\text{ cm}^{-1}$ , and  $V_n \sim 0\text{ cm}^{-1}$  in the excited state. The  $V_2$  term represents a potential cross term between the two methyl rotors. The use of a kinetic energy cross term with a weighting coefficient of 0.72 in the Hamiltonian is also required for an accurate description of the excited state of this isomer. Empirical force field (EFF) calculations are performed for toluene and the three xylenes using a molecular orbital-molecular mechanics (MOMM) algorithm. The EFF-MOMM calculations are in essential agreement with the spectroscopic results and the one-dimensional rigid rotor model.

## A study of nonrigid aromatic molecules by supersonic molecular jet spectroscopy. II. Propyltoluenes

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Dispersed emission (DE) and time of flight mass spectra (TOFMS) are presented for supersonic molecular jet-cooled *o*-, *m*-, and *p*-*n*-propyltoluene. The spectra exhibit multiple origins which are assigned to *anti* and *gauche* conformations of the propyl group relative to the aromatic ring. The TOFMS of *m*-*n*-propyltoluene rules out an eclipsed propyl conformation as a populated conformation. Empirical force field (EFF) calculations are presented which support these assignments. The spectra also exhibit features, typically within  $100\text{ cm}^{-1}$  of the origin, which are assigned to transitions associated with the internal rotation of the ring methyl group. A model which treats this methyl motion as a one-dimensional rigid rotor is used to solve for the rotational constant  $B$  of the methyl rotor, and for the size and shape of the barrier to rotation. The barrier for *p*-*n*-propyltoluene is found to be small in both the ground ( $S_0 - V_n = 5\text{ cm}^{-1}$ ) and excited ( $S_1 - V_n = 20\text{ cm}^{-1}$ ) electronic states. For *m*-*n*-propyltoluene, the ground state is again found to have a low barrier ( $V_n = 23\text{ cm}^{-1}$ ), but the excited state has a potential barrier of  $V_1 = 75\text{ cm}^{-1}$ . The barrier for *o*-*n*-propyltoluene in the ground state is observed to be higher ( $V_1 = 64\text{ cm}^{-1}$ ) than for the other two isomers. The first excited electronic state of this latter compound displays a multitude of levels in the TOFMS which are explained by a double-rotor model involving the ring methyl group ( $V_1 = 72\text{ cm}^{-1}$ ,  $V_n = -14\text{ cm}^{-1}$ ) and terminal methyl group of the propyl chain ( $V_1 = 106\text{ cm}^{-1}$ ,  $V_n = -13\text{ cm}^{-1}$ ). The results are indicative of an interaction between the ring methyl group and the propyl chain. In all three *n*-propyltoluene isomers, more than one origin peak is present in the TOFMS, indicating the presence of multiple stable propyl conformations for each isomer. The propyltoluenes thus demonstrate two types of nonrigid molecular behavior: internal rotational motion associated with the ring methyl group, and potentially three stable conformations of the propyl chain with respect to the aromatic ring.

**Torsional Motion in Aromatic Molecules.  
Conformational Analysis of Methyl-, Ethyl-, and  
*n*-Propylbenzenes<sup>1</sup>**

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To an ever increasing extent, information regarding torsional vibrations of organic molecules is being provided by theoretical treatments rather than by experimental observation.<sup>1</sup> When experimental data are available, all too frequently they pertain to mole fraction weighted averages of the individual contributing conformations rather than the individual conformations themselves.<sup>2</sup> We now demonstrate that supersonic molecular jet spectroscopy can provide a novel means (a) to determine experimental values for torsional potential barriers in  $S_0$  and  $S_1$ , (b) to "freeze out" molecular conformations which have very low (ca. 1–5 kcal mol<sup>-1</sup>) free energy barriers between themselves, (c) to "count" the number of stable ground state conformations and, by doing so, establish their molecular geometries, and (d) to observe spectroscopic properties of these individual conformations.

Much current interest exists in the conformational analysis of alkyl-substituted benzene substrates, and herein we focus specific attention on the first three members of this class of compounds: methyl, ethyl, and *n*-propyl. Both time of flight mass spectra (TOFMS) and dispersed emission (DE) spectra are determined for the systems studied.<sup>3</sup> Figure 1 presents the TOFMS of *m*-xylene (1) for the  $0_0^0$  region of the  $S_1 \leftarrow S_0$  transition. The various features of this spectrum are attributed to transitions between internal rotor states of the two methyl groups. A double one-dimensional rigid rotor model can be employed to fit these data.<sup>4–6</sup>

## van der Waals clusters of pyridazine and isoquinoline: The effect of solvation on chromophore electronic structure<sup>a)</sup>

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van der Waals clusters of pyridazine and isoquinoline with  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_3\text{OH}$  are generated in a supersonic molecular jet expansion and investigated by two-color time-of-flight mass spectroscopy. As is the case for the other diazine systems, no spectra could be observed for pyridazine  $(\text{H}_2\text{O})_n$  or  $(\text{CH}_3\text{OH})_n$  clusters. Both chromophore molecules are reported to have close lying, vibronically coupled  $S_1$  and  $S_2$  excited states:  $n\pi^*$  for pyridazine and  $n\pi^*$  ( $S_1$ ) and  $\pi\pi^*$  ( $S_2$ ) for isoquinoline. Cluster spectra for pyridazine methane and ammonia clusters do not favor the presence of two  $n\pi^*$  transitions in the  $S_1 \rightarrow S_0$  transition region but rather suggest that the " $S_2$  origin" is a vibronic feature of the  $S_1 \rightarrow S_0$  transition. Isoquinoline clusters that are only weakly or not at all hydrogen bonded ( $\text{CH}_4$  and  $\text{NH}_3$ ) display a complicated spectrum indicative of  $S_1$  ( $n\pi^*$ )– $S_2$  ( $\pi\pi^*$ ) vibronic coupling and not the usual shifted isolated molecular spectrum. Isoquinoline clusters with substantial hydrogen bonding ( $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$ ) display relatively simple spectra indicative of only a single electronic transition  $S_2$  ( $\pi\pi^*$ )  $\rightarrow S_0$  in the region and no interstate vibronic coupling. These results are compared and contrasted with each other and the spectra of the other diazine clusters. Potential energy calculations are also employed to help understand the clustering in these systems.

## Spectroscopic studies of cryogenic fluids: Benzene in argon and helium<sup>a)</sup>

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Energy shifts and bandwidths of the  $6_0^1$  vibronic feature of the  ${}^1B_{2u} \rightarrow {}^1A_{1g}$  optical absorption spectrum of benzene dissolved in supercritical argon and helium, and in liquid argon are reported as a function of pressure, temperature, and density. Benzene/Ar solutions display red shifts of the  $6_0^1$  transition with increasing density but the dependence is found to be nonlinear at high densities. Benzene/He solutions evidence blue shifts of the  $6_0^1$  transition as a function of increasing density which also becomes nonlinear at high densities. Only small spectral shifts are recorded if the density is kept constant and pressure and temperature are varied simultaneously. In addition, a small density independent temperature effect on the transition energy shift is identified. Experimental results are compared to dielectric (Onsager–Böttcher and Wertheim) and quantum statistical mechanical (Schweizer–Chandler) theories of solvent effects on solute absorption energy. Reasonably good agreement between experiment and theory is found only for the benzene/Ar system at relatively low densities. The theory fails to predict energy shifts for both the benzene/He and high density benzene/Ar systems. This result is different from the findings for the benzene/ $\text{N}_2$  and benzene/ $\text{C}_3\text{H}_8$  solutions and can be interpreted qualitatively in terms of competition between dispersive attractive and repulsive interactions as a function of density. The failure of the theory to describe these transition energy shifts is attributed to the omission of explicit repulsive interactions terms in the theoretical models employed.

# Supersonic molecular jet spectroscopy of ethylbenzene, the ethyltoluenes, and the diethylbenzenes

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Time-of-flight mass spectra are presented for the  $S_1 \leftarrow S_0$  origin region of jet-cooled 1,2-, 1,3-, and 1,4-diethylbenzene, and 2-, 3-, and 4-ethyltoluene. The spectra for the diethylbenzenes exhibit two origins which are assigned to *syn* and *anti* conformations of the ethyl groups relative to the aromatic ring. The existence of two origins in the 1,3-diethylbenzene spectrum, and only one in the 3-ethyltoluene spectrum, strongly implies that the stable orientation of the ethyl groups is with the  $\beta$ -carbon atom of the ethyl group projecting perpendicular to the plane of the aromatic ring. The size and shape of the potential barrier to rotation of the ring methyl group is obtained by treating the methyl group as a one-dimensional rigid rotor and fitting the calculated energy levels to observed features in the spectra. The results (for the para isomer  $B = 5.20 \text{ cm}^{-1}$ ,  $V_6 = 31.00 \text{ cm}^{-1}$ ; for the meta isomer,  $B = 5.40 \text{ cm}^{-1}$ ,  $V_3 = 78.00 \text{ cm}^{-1}$ ; and for the ortho isomer,  $B = 5.50 \text{ cm}^{-1}$ ,  $V_3 = 89.00 \text{ cm}^{-1}$ ) indicate that the methyl group experiences an increased barrier to rotation in the order para < meta < ortho isomer.

## Spectroscopic studies of phthalocyanines and their clusters with small molecules<sup>a)</sup>

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van der Waals clusters of free base phthalocyanine ( $H_2Pc$ ) and magnesium phthalocyanine ( $MgPc$ ) with small hydrocarbons [ $C_n H_{2n+2}$  ( $n = 1, 2, 3$ )], hydrogen bonding solvents ( $H_2O$ ,  $MeOH$ ,  $EtOH$ ), and  $CO_2$  are studied in the gas phase using supersonic molecular jet spectroscopy. Fluorescence excitation spectra of the cluster systems are characterized in the  $0_0^0$  regions of the cluster  $S_1 \leftarrow S_0$  transitions. Forbidden low frequency cluster chromophore out-of-plane vibronic transitions are induced by clustering in the majority of the cluster systems studied. This low frequency motion is characterized using an out-of-plane normal coordinate analysis on the  $H_2Pc$  moiety. Calculations of the binding energy and ground state geometry for the clusters are carried out employing Lennard-Jones (6-12-1) and hydrogen bonding (10-12-1) potentials. Comparison between the calculations and experiments allow for the identification of specific configurations responsible for the cluster vibronic transitions observed. The cluster vibronic spectra and theoretical calculations suggest that stable  $H_2Pc$  and  $MgPc$  solvation sites are located over the phthalocyano core and not over peripheral ring centers. The  $H_2Pc$ /hydrocarbon cluster experimental and calculational results parallel those obtained for benzene and *N*-heterocycle/hydrocarbon clusters studied previously. The  $H_2Pc$  and  $MgPc$ /alcohol cluster spectra and calculated geometries suggest that the solvent OH group is intimately involved in the intermolecular interactions and contributes significantly to the observed spectroscopic shifts.

## Observation and Geometry Assignment of Individual Conformations of Aryl Methyl Ethers in the Gas Phase

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Supersonic molecular jet laser spectroscopy is used to observe the individual conformations of a number of aryl methyl ethers in the gas phase and to establish their planar conformations.

Aromatic methyl ethers continue to play an important role in organic chemistry. This functionality has much synthetic utility and is frequently found in natural products, including many compounds of pharmacological value. The study of the potential energy profiles of this functional group has added significance in terms of regiochemistry; e.g., kinetic electrophilic attack on the aromatic ring system of (1) is a function of  $\pi$ -electron density which itself is modified by methoxy conformer distributions.<sup>1</sup> Results from sophisticated experimental and theoretical investigations have been interpreted in terms of planar conformations (*cf.* Scheme 1), though exceptions have been noted and definitive evidence is not available.<sup>2-7</sup>

As part of our studies<sup>8,9</sup> on the conformations and reactivities of aromatic compounds in the gas phase and in clusters, we have examined the supersonic molecular jet laser spectroscopy of anisole and some of its derivatives. The various techniques associated with supersonic molecular jet laser spectroscopy [including one and two colour time of flight mass spectroscopy (TOFMS), fluorescence excitation (FE), and dispersed emission (DE) spectroscopy] employed in these investigations have recently been reported.<sup>9</sup> Consider an aromatic molecule. The energy of the  $\pi \rightarrow \pi^*$  electronic transition ( $S_1 \leftarrow S_0$ ) for each stable conformation of the molecule will, in principle, generate its own spectroscopic (0<sup>0</sup>) transition (origin transition). The converse is also true; i

## Spectroscopy and Structure of 2-Hydroxyquinoline

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The two-photon time-of-flight mass spectroscopy (TOFMS), fluorescence excitation spectrum, and dispersed emission spectra of 2-hydroxyquinoline are reported. Absorption and emission spectra from both the lactim (2-hydroxyquinoline) and the lactam (2(1H)-quinolone) tautomers are observed. The origins for the lactam and lactim forms are 29 112 and 31 349  $\text{cm}^{-1}$ , respectively. No evidence of excited-state proton transfer in the lactim with up to 2800  $\text{cm}^{-1}$  of excess vibrational energy can be found.

## Chemical reactions in isolated clusters: Excited state electron transfer in 3- and 4-dimethylaminobenzonitrile<sup>a)</sup>

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Two-color time-of-flight mass spectra of 3- and 4-dimethylaminobenzonitrile (3- and 4-DMABN) bare molecules and clusters with methane, water, acetone, dichloromethane, and acetonitrile are reported and discussed. The clusters and molecules are isolated and cooled in a supersonic expansion. Both 3- and 4-DMABN bare molecules display significant changes in geometry, associated with rotation-inversion coordinates of the dimethylamino group, upon excitation from the ground electronic state  $S_0$  to the first excited singlet state  $S_1$ . Cluster spectra for the monosolvates [ $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $(\text{CH}_3)_2\text{CO}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$ ] of 3- and 4-DMABN evidence two general types of behavior. (1) Cluster spectra have both red and blue shifts from their respective bare molecule origins which are relatively small (in general less than  $200\text{ cm}^{-1}$ ). These cluster spectra are nearly identical with the bare molecule spectra; the solvation process seems to have little effect on the DMABN molecule, especially the  $-\text{N}(\text{CH}_3)_2$  moiety, for these clusters or cluster states. (2) Cluster spectra have shifts that are large ( $\sim 500$ – $1000\text{ cm}^{-1}$ ) and to low energy of the bare molecule spectra. These cluster spectra are composed of both sharp and broad features which bear little resemblance to those observed in the respective bare DMABN molecule spectra. Results of calculations of cluster geometry suggest that the different cluster spectra may be associated with clusters of different geometry. These data are interpreted in terms of solution behavior of 3- and 4-DMABN. The relationship between the twisted intramolecular charge transfer (TICT) state model proposed for 4-DMABN in dipolar aprotic solvents and these cluster results is explored.

## Geometry and torsional motion of biphenyl in the ground and first excited singlet state

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The lowest excited singlet state of biphenyl (BP) and a number of its isotopically and chemically substituted analogs have been studied by supersonic jet laser spectroscopy. The symmetry species of this excited state in BP can be classified as  $B_{2u}^+$  in the  $G_{16}$  extended molecular symmetry group  $G_{16}$  (EM). The symmetry-allowed origin of the biphenyl  $-h_{10}$   $S_1 - S_0$  electronic transition occurs at  $35\,268\text{ cm}^{-1}$ . The frequency of the torsional motion in  $S_1$  is determined to be  $\sim 65\text{ cm}^{-1}$ . The potential parameters for this motion in  $S_1$  are  $V_2 = 1195\text{ cm}^{-1}$ ,  $V_4 = -190\text{ cm}^{-1}$ , and  $V_6 = 18\text{ cm}^{-1}$ . The torsional motion for the ground state ( $\sim 50\text{ cm}^{-1}$ ) can be described by  $V_2 = 50\text{ cm}^{-1}$  and  $V_4 = -148\text{ cm}^{-1}$ . The change in the dihedral angle between the two benzene rings in BP upon  $S_0$  to  $S_1$  excitation is determined to be  $\sim 44^\circ$  based on a Franck-Condon factor calculation. Several fundamentals of the molecular vibrations are assigned in the  $S_1$  state. The exciton interaction between the coupled benzene rings in biphenyl is suggested to be large ( $> 10^3\text{ cm}^{-1}$ ).



# Benzene clustered with N<sub>2</sub>, CO<sub>2</sub>, and CO: Energy levels, vibrational structure, and nucleation

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Two-color time-of-flight mass spectroscopy is employed to study the van der Waals (vdW) clusters of benzene(N<sub>2</sub>)<sub>n</sub> ( $n \leq 8$ ), benzene(CO<sub>2</sub>)<sub>n</sub> ( $n \leq 7$ ), and benzene(CO)<sub>n</sub> ( $n = 1, 2$ ) created in a supersonic molecular jet. Potential energy calculations of cluster geometries, normal coordinate analysis of vdW vibrational modes, and calculations of the internal rotational transitions are employed for the assignment of the benzene(solvent)<sub>1</sub> cluster spectra in the 0<sub>0</sub><sup>0</sup> and 6<sub>0</sub><sup>1</sup> regions of the benzene <sup>1</sup>B<sub>2u</sub> - <sup>1</sup>A<sub>1g</sub> transition. The respective vibronic and rotational selection rules for these clusters are determined based on the appropriate point groups and molecular symmetry groups of the clusters. Good agreement between the calculated and experimental spectra is obtained with regard to the vdW vibrational and internal rotational modes. The solvent molecules rotate nearly freely with respect to benzene about the benzene-solvent bond axis in the benzene(solvent)<sub>1</sub> clusters. In the excited state a small ~20 cm<sup>-1</sup> barrier to rotation is encountered. Studies of larger clusters ( $n > 2$ ) reveal a broad red shifted single origin in the 6<sub>0</sub><sup>1</sup> spectra. A linearly increasing cluster energy shift is observed as a function of cluster size. The cluster energy shifts are not saturated by one solvent molecule on each side of the aromatic ring; several solvent molecules effectively interact with the solute  $\pi$  electronic cloud. Both homogeneous and inhomogeneous nucleation take place for the clusters studied depending on the ratio of the solvent-solvent binding energy to the cluster binding energy.

A Study of Non-Rigid Aromatic Molecules. Observation and  
Spectroscopic Analysis of the Stable Conformations of Various  
Alkylbenzenes by Supersonic Molecular Jet Laser Spectroscopy

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**Abstract:** The technique of supersonic molecular jet laser spectroscopy was used to determine the stable conformations of a series of alkylbenzenes. This study demonstrates, for the first time, the sensitivity of molecular jet spectroscopy in determining both the number of stable conformations as well as the geometry of various ethyl, propyl and butyl substituents relative to the aromatic ring. Different rotamers with low barriers to interconversion, < 5 kcal/mole, can be isolated in the supersonic jet expansion. Each observed conformation exhibits its own spectroscopic origin ( $S_1 \leftarrow S_0$  transition) in a 2-color time-of-flight mass spectrum (TOFMS). The number of stable conformations is then used to determine the minimum energy geometries of the substituent group. Previous identification of individual molecular conformations for such low barriers to interconversion has not been attainable with conventional techniques such as variable temperature NMR.

# Observation and Geometry Assignment of Individual Conformations of Aryl Methyl Ethers in the Gas Phase

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Supersonic molecular jet laser spectroscopy is used to observe the individual conformations of a number of aryl methyl ethers in the gas phase and to establish their planar conformations.

Aromatic methyl ethers continue to play an important role in organic chemistry. This functionality has much synthetic utility and is frequently found in natural products, including many compounds of pharmacological value. The study of the potential energy profiles of this functional group has added significance in terms of regiochemistry; *e.g.*, kinetic electrophilic attack on the aromatic ring system of (1) is a function of  $\pi$ -electron density which itself is modified by methoxy conformer distributions.<sup>1</sup> Results from sophisticated experimental and theoretical investigations have been interpreted in terms of planar conformations (*cf.* Scheme 1), though exceptions have been noted and definitive evidence is not available.<sup>2-7</sup>

As part of our studies<sup>8,9</sup> on the conformations and reactivities of aromatic compounds in the gas phase and in clusters, we have examined the supersonic molecular jet laser spectroscopy of anisole and some of its derivatives. The various techniques associated with supersonic molecular jet laser spectroscopy [including one and two colour time of flight mass spectroscopy (TOFMS), fluorescence excitation (FE), and dispersed emission (DE) spectroscopy] employed in these investigations have recently been reported.<sup>9</sup> Consider an aromatic molecule. The energy of the  $\pi \rightarrow \pi^*$  electronic transition ( $S_1 \leftarrow S_0$ ) for each stable conformation of the molecule will, in principle, generate its own spectroscopic  $0^0$  transition (origin transition). The converse is also true: *i*

## DETERMINATION OF THE MINIMUM ENERGY CONFORMATION OF ALLYL BENZENE AND ITS CLUSTERS WITH METHANE, ETHANE, WATER AND AMMONIA

### Abstract

Supersonic molecular jet laser time of flight mass spectroscopy (TOFMS) is employed to determine the minimum energy conformation of the allyl group with respect to the benzene ring of allylbenzene, 1-allyl-2-methylbenzene and 1-allyl-3-methylbenzene. The spectra are assigned and conformations are suggested with the aid of molecular orbital molecular mechanics (MOMM-85) calculations. Based on the experimental and theoretical results, the minimum energy conformer is found to have  $\tau_1(\text{C}_{\text{ortho}}-\text{C}_{\text{ipso}}-\text{C}_{\alpha}-\text{C}_{\beta}) = \text{ca. } 90^\circ$  (*i.e.*, the allyl group is essentially perpendicular to the plane of the benzene ring) and  $\tau_2(\text{C}_{\text{ipso}}-\text{C}_{\alpha}-\text{C}_{\beta}-\text{C}_{\gamma}) = \pm 120^\circ$  (*i.e.*, the olefin C=C bond is eclipsed with the  $\text{C}_{\alpha}-\text{H}_{\alpha}$  bond). The TOFMS of allylbenzene clustered with methane, ethane, water and ammonia are also presented. A Lennard-Jones potential energy 6-12-1 atom-atom calculation is used to characterize the structures of these clusters. Experiments and calculations demonstrate that the four different solvent molecules studied can form stable clusters with allylbenzene by coordinating to the  $\pi$ -system of the allyl substituent in addition to that of the aromatic ring.

## Spectroscopy, Structure, and Proton Dynamics of 2-Hydroxypyridine and Its Clusters with Water and Ammonia

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The two tautomeric forms of 2-hydroxypyridine (2-HP) have been studied in a supersonic jet expansion. Time-of-flight mass spectroscopy (TOFMS) and emission spectroscopy of the lactim and lactam tautomers have been studied and are reported here. The lactim spectrum is similar to an earlier TOFMS spectrum and has its origin at  $36\,136\text{ cm}^{-1}$ . Evidence of mixing of the  $\pi\pi^*$  and  $\pi\pi^*$  electronic states is seen in the lactim spectrum. The mixing is removed in the disolvate water cluster but not in monosolvate clusters of ammonia or water. The lactam is shown to be nonplanar giving rise to two origins in the excitation spectrum at  $29\,832$  and  $29\,935\text{ cm}^{-1}$ . The ammonia and water lactim cluster spectra show significant shifts to the red while the cluster spectra to the lactam show large shifts to the blue. Experimental evidence for strong hydrogen bonding in these clusters is discussed. Intramolecular and intermolecular proton transfer in 2-HP and its clusters is discussed in the context of these data.

## Spectroscopic Observation and Geometry Assignment of the Minimum Energy Conformations of Methoxy-Substituted Benzenes

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**Abstract:** Optical spectroscopic data are presented for methoxybenzene, the three methoxytoluenes, 1-ethyl-4-methoxybenzene, and 1,2- and 1,3-dimethoxybenzene cooled and isolated in a supersonic jet expansion. Each unique stable conformation of the sterically unencumbered methoxybenzenes displays a unique and assignable spectrum; the interpretation of these spectra leads to the assignment of specific molecular geometries for each system. The minimum energy conformation of the methoxy group with respect to the ring is shown to be a planar conformation in which the methoxy group lies in the plane of the ring. The potential barrier for rotation of the ring methyl group in the methoxytoluenes is characterized from observed transitions between methyl group rotational levels which accompany the electronic transition. The meta isomer exhibits a large barrier to methyl rotation in  $S_1$  ( $V_3 \sim 520\text{ cm}^{-1}$ ) whereas the methyl group in the ortho and para isomers is nearly freely rotating ( $V_3 \leq 50\text{ cm}^{-1}$ ). The dimethoxybenzenes exhibit spectral features due to torsions of the methoxy groups. Substantial barriers to methoxy group rotation ( $V_1 = 500\text{ cm}^{-1}$ ,  $V_2 = 100\text{ cm}^{-1}$  for ortho,  $V_1$  and  $V_2 \sim 2000\text{--}5000\text{ cm}^{-1}$  for meta) are established; again the torsional barrier appears to be highest for the meta or 3-position on the ring. The presence of cross kinetic and potential terms between methoxy groups is further suggested for the ortho isomer.

CONFORMATIONAL CHANGES UPON  $S_1 \leftarrow S_0$  EXCITATION IN  
4-DIMETHYLAMINOBENZONITRILE AND SOME OF ITS CHEMICAL ANALOGS

ABSTRACT

One-color time-of-flight mass spectra (mass resolved excitation spectra) for jet-cooled 4-dimethylaminobenzonitrile (4-DMABN) and some of its chemical analogs, dimethylaniline (DMA), 3-dimethylaminobenzonitrile (3-DMABN), N,N-dimethyl-4-(trifluoromethyl)benzamine (4-CF<sub>3</sub>-DMA) and 4-(d<sub>8</sub>-dimethylamino)benzonitrile (4-d<sub>8</sub>-DMABN), are presented and analyzed. Near the origin of the  $S_1 \leftarrow S_0$  transition the low frequency modes can be assigned to motions of the dimethylamino group for this series of molecules. The inversion motion of the dimethylamino group and the dimethylamino group torsion about the C<sub>ipso</sub>-N bond (the twist coordinate) in  $S_1$  give rise to the most prominent peaks in this spectrum. The potential parameters for the twist coordinate of 4-DMABN and DMA are quite similar in  $S_1$ :  $B = 0.546$ ,  $V_2 = 175$ , and  $V_4 = 525 \text{ cm}^{-1}$  for 4-DMABN and  $B = 0.546$ ,  $V_2 = 175$ , and  $V_4 = 515 \text{ cm}^{-1}$  for DMA. The  $V_2$  and  $V_4$  terms are slightly larger for 3-DMABN and 4-CF<sub>3</sub>-DMA. The inversion motion is also similar for these molecules but is more anharmonic for the para-substituted dimethylanilines, 4-DMABN and 4-CF<sub>3</sub>-DMA, than for the meta and unsubstituted molecules. A Franck-Condon intensity analysis for the dimethylamino twist in these molecules suggests that this group in 4-DMABN is displaced in the excited state by ca. 30° with respect to its planar orientation in the ground state. In both solutions and monosolvate clusters of 4-DMABN with polar aprotic solvents, a low lying charge transfer (CT) state is identified in addition to the usual  $\pi^*$  excited state of the bare molecule. The relation between the bare molecule-4-DMABN twisting displacement upon excitation and the low lying CT state is discussed.

# SPECTROSCOPY AND STRUCTURE OF JET-COOLED ALPHA-METHYLSTYRENE

## ABSTRACT

The sterically hindered styrene derivative,  $\alpha$ -methylstyrene (2-phenylpropane), is studied by 1-color time-of-flight mass spectroscopy (TOFMS). In contrast to styrene, which has an intense spectral origin transition in the TOFMS,  $\alpha$ -methyl styrene exhibits a weak origin transition. A progression in a low frequency torsional mode, with an energy level spacing of  $\sim 69 \text{ cm}^{-1}$ , is built on the origin. The intensity maximum of this progression occurs at the eighth peak position, indicating that the ground and excited state geometries are displaced from one another. The torsional progression is assigned to the hindered rotation of the propenyl group with respect to the aromatic ring. Potential parameters derived from an analysis of the spectra are  $V_2 = 0.0$  and  $V_4 = 150.0 \text{ cm}^{-1}$  for  $S_0$  and  $V_2 = 4867$ ,  $V_4 = -500$  and  $V_6 = -80 \text{ cm}^{-1}$  for  $S_1$ . Based on hot band transitions in the region of the origin, this torsional mode is assigned an energy level spacing of  $\sim 32 \text{ cm}^{-1}$  in the ground state. In the ground state the propenyl group is calculated to be at a  $\sim 31^\circ$  angle from the plane of the aromatic ring. Analysis of the Franck-Condon intensity profile yields a displacement in the excited state, for the angle between the aromatic and ethylenic groups, of  $30^\circ$  relative to the ground state. Alpha-methylstyrene is suggested to be nearly planar in its first excited  $\pi\text{-}\pi^*$  state.

A CONFORMATIONAL STUDY OF JET-COOLED STYRENE DERIVATIVES.

DEMONSTRATION OF THE PLANARITY OF NON-STERICALLY HINDERED STYRENES.

ABSTRACT

One-color time-of-flight mass spectroscopy (mass resolved excitation spectroscopy) is used to determine ground and excited state geometries and molecular parameters for styrene and a number of its derivatives cooled in a supersonic jet expansion. In this paper we present results for styrene and a series of sterically unhindered substituted derivatives: trans- $\beta$ -methylstyrene, 3-methylstyrene, 4-ethylstyrene and 4-methoxy-trans- $\beta$ -methylstyrene (anethole). Styrene, trans- $\beta$ -methylstyrene and 4-ethylstyrene all exhibit one spectroscopic origin corresponding to a single conformation, whereas 3-methylstyrene and anethole exhibit two origins corresponding to syn and anti ground state conformations. The vinyl group is concluded to be planar with respect to the aromatic ring for all of these molecules in both  $S_0$  and  $S_1$ . A one-dimensional methyl rotor analysis for the two conformers of 3-methylstyrene in the first excited singlet state  $S_1$  yields the parameters for methyl rotation in the anti conformer,  $B = 5.20$ ,  $V_3 = 80.0$  and  $V_6 = -15.0 \text{ cm}^{-1}$  and in the more hindered syn conformer,  $B = 5.95$ ,  $V_3 = 185.0$  and  $V_6 = -27.5 \text{ cm}^{-1}$ .

Observation and Geometry Assignment of Conformations of Styrenes  
in the Ground and First Excited Singlet State

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**Abstract:** The technique of supersonic molecular jet laser spectroscopy is used to determine the stable conformations of a series of sterically unhindered styrenes and of  $\alpha$ -methylstyrene. This study demonstrates, for the first time, that the most stable ground state conformation of unhindered styrenes is the all-planar geometry. Spectroscopic origin transitions were observed in the time of flight mass spectra (TOFMS) for the two (anti and syn) planar conformations of anethole [4-methoxy-1-(1E-propenyl)benzene]. The TOFMS of the unhindered styrenes typically consists of a very strong  $0_0^0$  transition and minor other transitions, if any. In contrast, the TOFMS of  $\alpha$ -methylstyrene exhibits a weak  $0_0^0$  transition and a progression in a low frequency torsional mode with an energy level spacing of  $69\text{ cm}^{-1}$ , with a maximum intensity at the eighth peak position. Franck-Condon intensity analysis yields a displacement for the torsional angle  $\tau(\text{C}_{\text{ortho}}-\text{C}_{\text{ipso}}-\text{C}_{\alpha}-\text{C}_{\beta})$   $\approx 30^\circ$  between the stable conformations in  $S_0$  and  $S_1$ , suggesting that  $\alpha$ -methylstyrene is twisted ca.  $30^\circ$  out of the plane in  $S_0$ .



## **A SPECTROSCOPIC CONFORMATIONAL STUDY OF ETHOXYBENZENE**

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An investigation of jet cooled ethoxybenzene and various substituted ethoxybenzenes, utilizing the techniques of one color time-of-flight mass spectroscopy and dispersed emission spectroscopy, is presented. Analysis of the accumulated data indicate that, under the conditions of our supersonic expansion, only one molecular conformation is present. The observations are consistent with an orientation placing the entire ethoxy group in the plane of the aromatic ring. These results are similar to those found for methoxybenzene.

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